10 Vibrations in diatomic molecules

10.1 Separation of internal and center of mass motion

In this section we will study how to apply the harmonic oscillator model to a diatomic molecule. The first aspect we have to study is how to connect the Hamiltonian of a diatomic molecule to that of the harmonic oscillator. For a diatomic molecule the Hamiltonian will depend on the coordinate of atom 1 (x_1) and atom 2 (x_2), as well as, their corresponding masses m_1 and m_2. The kinetic energy is

$$\hat{T} = -\frac{\hbar^2}{2m_1}\frac{\partial^2}{\partial x_1^2} + -\frac{\hbar^2}{2m_2}\frac{\partial^2}{\partial x_2^2}, \tag{1}$$

while the potential is

$$\hat{V} = \frac{1}{2}k(x_2 - x_1 - r_e)^2, \tag{2}$$

where we assumed that the potential is $(x_2 - x_1 - r_e)^2$ is the square of the distance of the two atoms. This potential is zero at the equilibrium bond distance, when $x_2 - x_1 = r_e$, otherwise it is positive. Now we will introduce two new variables, the bond distance (r) and the center of mass (R), defined as

$$r = x_2 - x_1 \tag{3}$$

$$R = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} = \frac{m_1 x_1 + m_2 x_2}{M}, \tag{4}$$

where $M = m_1 + m_2$ is the total mass.

In this new system of coordinates the potential simplifies to

$$\hat{V} = \frac{1}{2}k(x_2 - x_1 - r_e)^2 = \frac{1}{2}k(r - r_e)^2, \tag{5}$$

Applying the chain rule we express the derivatives in x_1 and x_2 as derivatives in r and R

$$\frac{\partial}{\partial x_1} = \frac{\partial r}{\partial x_1}\frac{\partial}{\partial r} + \frac{\partial r}{\partial x_1}\frac{\partial}{\partial r}, \tag{6}$$

where

$$\frac{\partial r}{\partial x_1} = \frac{\partial}{\partial x_1}(x_2 - x_1) = -1, \tag{7}$$

and

$$\frac{\partial R}{\partial x_1} = \frac{\partial}{\partial x_1}\left(\frac{m_1 x_1 + m_2 x_2}{m_1 + m_2}\right) = \frac{m_1}{M}. \tag{8}$$

So we can write

$$\frac{\partial}{\partial x_1} = -\frac{\partial}{\partial r} + \frac{m_1}{M}\frac{\partial}{\partial R}, \tag{9}$$

and the second derivative is

$$\frac{\partial^2}{\partial x_1^2} = \frac{\partial^2}{\partial r^2} + \left(\frac{m_1}{M}\right)^2\frac{\partial^2}{\partial R^2} - \frac{2m_1}{M}\frac{\partial^2}{\partial R\partial r}. \tag{10}$$

Repeating the same for x_2 we get

$$\frac{\partial^2}{\partial x_2^2} = \frac{\partial^2}{\partial r^2} + \left(\frac{m_2}{M}\right)^2\frac{\partial^2}{\partial R^2} + \frac{2m_2}{M}\frac{\partial^2}{\partial R\partial r}. \tag{11}$$

Plugging these two derivatives in the kinetic energy operator we get

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left[\frac{\partial^2}{\partial r^2} + \left(\frac{m_1}{M}\right)^2 \frac{\partial^2}{\partial R^2} - \frac{2m_1}{M}\frac{\partial^2}{\partial R \partial r}\right] \tag{12}$$

$$-\frac{\hbar^2}{2m_2}\left[\frac{\partial^2}{\partial r^2} + \left(\frac{m_2}{M}\right)^2 \frac{\partial^2}{\partial R^2} + \frac{2m_2}{M}\frac{\partial^2}{\partial R \partial r}\right] \tag{13}$$

$$= -\frac{\hbar^2}{2}\frac{\partial^2}{\partial R^2}\left(\frac{m_1}{M^2} + \frac{m_2}{M^2}\right) - \frac{\hbar^2}{2}\frac{\partial^2}{\partial r^2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \tag{14}$$

$$= -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}. \tag{15}$$

The quantity μ is called the **reduced mass**

$$\mu = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2}. \tag{16}$$

Putting all together we can write the Hamiltonian as

$$\hat{H} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{1}{2}k(r - r_e)^2 = \hat{H}_{\text{CM}} + \hat{H}_{\text{HO}}, \tag{17}$$

which we separated as a center-of-mass Hamiltonian (CM) and a harmonic oscillator Hamiltonian (HO),

$$\hat{H}_{\text{CM}} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}, \tag{18}$$

and

$$\hat{H}_{\text{HO}} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{1}{2}k(r - r_e)^2. \tag{19}$$

Recall that the center-of-mass Hamiltonian is the same as that for a particle in a box. So we can solve this problem for a particle in a box of dimension L much larger than the molecule bond length.

Note that the Hamiltonian can be written as a sum of two separate terms that act on different coordinates. The center-of-mass Hamiltonian ($\hat{H}_{\text{CM}}$) depends only on R, while the harmonic oscillator Hamiltonian ($\hat{H}_{\text{HO}}$) acts only on r. In this case we say that the Hamiltonian is **separable,** and the eigenvalues and eigenfunctions are related to those of the two separate Hamiltonians.[1] The eigenvalues are the sum of the eigenvalues for a particle in a box (of mass M and length L) and a harmonic oscillator (with $\omega = \sqrt{\frac{k}{\mu}}$)

$$E_{n,v} = E_n^{\text{CM}} + E_v^{\text{HO}} = \frac{h^2 n^2}{8ML^2} + \hbar\omega\left(v + \frac{1}{2}\right) \tag{20}$$

The eigenfunctions are instead given by

$$\psi(R, r) = \psi_n^{\text{PIB}}(R)\psi_v^{\text{HO}}(r), \tag{21}$$

where $\psi_n^{\text{PIB}}(R)$ and $\psi_v^{\text{HO}}(r)$ are the eigenfunctions for a particle in a box and a harmonic oscillator, respectively.

10.2 Selection rule and vibrational spectra

If we are interested in the vibrational spectroscopy of diatomic molecules we can focus exclusively on the v dependence of the energy.

Not all transitions between the energy levels of the harmonic oscillator are allowed. The **selection rule**[2] for a harmonic oscillator tells us that the only allowed transitions are those

[1]In general, if the Hamiltonian splits into two parts $\hat{H} = \hat{H}_A + \hat{H}_B$, where $\hat{H}_A$ and $\hat{H}_B$ act on different variables x and y, then the eigenvalues and eigenfunctions of $\hat{H}$ are $E = E_A + E_B$ and $\psi(x, y) = \psi_A(x)\psi_B(y)$, where $\hat{H}_A\psi_A(x) = E_A\psi_A(x)$ and $\hat{H}_B\psi_B(x) = E_B\psi_B(x)$.

[2]Selection rules can be justified with quantum mechanics, but this subject is a bit advanced and will be covered later

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that satisfy

$$\Delta v = \pm 1. \tag{22}$$

Absorption of a photon can promote a harmonic oscillator from the level v to $v + 1$. The energy of the photon corresponding to this transition is given by the energy difference of these two levels

$$\Delta E_v = E_{v+1} - E_v = \hbar\omega \left(v + 1 + \frac{1}{2} \right) - \hbar\omega \left(v + \frac{1}{2} \right) = \hbar\omega, \tag{23}$$

where

$$\omega = \hbar\sqrt{\frac{k}{\mu}}. \tag{24}$$

Note that this difference is independent of v, so all transitions of a harmonic oscillator occur at the same frequency.

■ Example 10.1 (Vibrations of diatomics).
The force constant of $H^{127}I$ is $k = 291 \text{N m}^{-1}$. Calculate the vibrational frequency of $H^{127}I$ in cm^{-1}.
 Solution: The energy difference between two level of the harmonic oscillator is

$$E = \hbar\omega = \hbar\sqrt{\frac{k}{\mu}}, \tag{25}$$

and the wave numbers corresponding to this transition are

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{E}{hc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}. \tag{26}$$

The reduced mass of $H^{127}I$ is

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.007825 \times 126.904468}{1.007825 + 126.904468} 1.660539040 \times 10^{-27} \text{kg} = 1.66035 \times 10^{-27} \text{kg} \tag{27}$$

Plugging the number in we get

$$\tilde{\nu} = \frac{1}{2\pi \times 299\,792\,458\,\text{m s}^{-1}} \sqrt{\frac{291\,\text{N m}^{-1}}{1.66035 \times 10^{-27}\text{kg}}} = 222\,252\,\text{m}^{-1} = 2222.52\,\text{cm}^{-1} \tag{28}$$

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10.3 The Morse potential

A convenient approximation to the potential of a diatomic molecule is the Morse potential

$$V(r) = D \left[1 - e^{-\beta(r-r_e)} \right]^2. \tag{29}$$

This potential contains two parameters. The first one, D, is the dissociation energy of the molecule, while r_e is the equilibrium bond distance. Both D and β are assumed to be positive.
 To find the equilibrium geometry for the Morse potential we take the first derivative and set it to zero

$$\frac{dV(r)}{dr} = 2D \left[1 - e^{-\beta(r-r_e)} \right] \frac{d}{dr} \left[1 - e^{-\beta(r-r_e)} \right] = 2D\beta \left[1 - e^{-\beta(r-r_e)} \right] e^{-\beta(r-r_e)}. \tag{30}$$

Setting the first derivative to zero requires solving the following equation

$$2D\beta \left[1 - e^{-\beta(r-r_e)} \right] e^{-\beta(r-r_e)} = 0 \tag{31}$$

This expression is zero when $r = r_e$. To see this substitute r with r_e in the term in square brackets

$$1 - e^{-\beta(r_e - r_e)} = 1 - e^0 = 1 - 1 = 0. \tag{32}$$

Once we know the equilibrium bond distance we can compute the dissociation energy (D_e) of the Morse potential. This quantity is defined as

$$D_e = V(\infty) - V(r_e). \tag{33}$$

The first term is equal to

$$V(\infty) = \lim_{r \to \infty} D \left[1 - e^{-\beta(r - r_e)}\right]^2 = D, \tag{34}$$

while the second one is equal to

$$V(r_e) = D \left[1 - e^{-\beta(r_e - r_e)}\right]^2 = 0. \tag{35}$$

So we find that for the Morse potential the dissociation energy is equal to the constant D

$$D_e = D. \tag{36}$$

The second derivative of the Morse potential is given by

$$\begin{aligned}
\frac{d^2 V(r)}{dr^2} &= 2D\beta \frac{d}{dr} \left[1 - e^{-\beta(r - r_e)}\right] e^{-\beta(r - r_e)} \\
&= 2D\beta \left[\beta e^{-2\beta(r - r_e)} - \beta \left[1 - e^{-\beta(r - r_e)}\right] e^{-\beta(r - r_e)}\right] \\
&= 2D\beta^2 \left[2e^{-2\beta(r - r_e)} - e^{-\beta(r - r_e)}\right].
\end{aligned} \tag{37}$$

The force constant for the Morse potential is the second derivative evaluated at the equilibrium bond distance, $r = r_e$

$$k = \left.\frac{d^2 V(r)}{dr^2}\right|_{r = r_e} = 2D\beta^2. \tag{38}$$